SYNTHESIS AND CHARACTERISATION

OF

SILICA COATED MAGNETITE NANOPARTICLE

A Dissertation
Submitted in partial fulfillment
FOR THE DEGREE OF
MASTER OF SCIENCE IN CHEMISTRY

Under The Academic Autonomy
NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

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CERTIFICATE

This is to certify that the dissertation entitled **"Synthesis and characterization of silica coated magnetite nanoparticle"** being submitted by Miss Ranjana Panigrahi to the Department of Chemistry, National Institute of Technology, Rourkela, Orissa, for the award of partial fulfillment of the degree of Master of Science is a record of the research training carried out by her under my supervision and guidance. This work is a scale-up synthesis process of silica coated magnetite following the procedure earlier reported. The matter embodied in the dissertation has not been submitted to any other University / Institute for the award of any Degree or Diploma.

Rourkela
Date: 05-05-2011

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Thanking you

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Abstract

Magnetite nanoparticle was prepared by co-precipitation of Fe^{2+} and Fe^{3+}, and then it was coated with silica. The silica coated magnetite nanoparticles were characterized in terms of their structure, morphology, hydrodynamic size and presence of surface functional groups by X-ray diffraction analysis, Scanning electron microscopy, Dynamic light scattering and Infrared spectroscopy respectively. It was found that the silica coating prevents magnetic particles from aggregation and imparts excellent stability in aqueous medium.

Chapter-1

INTRODUCTION

Nanoscience is one of the most important research & development frontiers in modern science. The use of nanoparticles offers many advantages due to their unique size & physical properties. Key importance of these magnetic nanoparticles is their unique properties [1], their controlled dimension maintaining their physical properties. Characteristics of magnetic nanoparticles such as high magnetization, superparamagnetism, high field irreversibility , high saturation field[2], smaller size than 100 nm and its narrow particle size distribution found to be advantageous for many technological applications such as for bio separation in life science[3] biomedicine and bioengineering such as magnetically assisted drug delivery [4], cell isolation [5], MRI contrast agents [6], immunoassay [7] and bio macromolecule purification [8]

Magnetic nanoparticle is an interesting system in nanotechnology applications due to the magnetic switching behavior and because of the transition between SPM and FM behaviors, which can be adjusted by modifying the distance between the particles. Nanoparticles possessing magnetic properties offer great advantages in that they can provide selective attachment to a functional molecule, confer magnetic properties to the target, and allow manipulation and transportation to a desired location through the control of a magnetic field produced by an electromagnet or permanent magnet. The important physical property that provides its wide application is its chemical inertness and resistance to surface oxidation.

The materials used in bio separation processes are superparamagnetic, meaning that they respond strongly to magnetic fields, but retain no residual magnetism after the field is removed. The morphology, surface area and the magnetic susceptibility of the support contribute in a major fashion to the efficiency of the separation processes. Additionally, the chemical nature of the support surface can be used to specify the separation process: the adsorption of the molecular species can be driven by the interactions at the molecular level between the surface groups of the paramagnetic particles and those of the target molecules.[9]

The surface of magnetite nanoparticle can be modified with several polymers such as polyethylene glycol [10], Polystyrene [11], starch [12], chitosan [13], inorganic chemicals such as SiO_2,ZrO_2,TiO_2. Coating of magnetic nanoparticles with silica is becoming a promising and

important approach in the development of magnetic nanoparticles for both fundamental study and technology application. First, silica formed on the surface of magnetic nanoparticles could screen the magnetic dipolar attraction between magnetic nanoparticles, which favors the dispersion of magnetic nanoparticles in liquid media and protects them from leaching in an acidic environment. Second, due to the existence of abundant silanol groups on the silica layer, silica-coated magnetic nanoparticles could be easily activated to provide the surface of silica-coated magnetic nanoparticles with various functional groups. Finally, the most important is that the silica layer provides a chemically inert surface for magnetic nanoparticles in biological systems [14].

Recently much attention has been focused on the development of suitable method or improvement of existing methods for large scale production of silica coated magnetic nanoparticles with reliable size, colloidal stability and good magnetic property. In the present dissert, we have synthesized magnetite nanoparticles by coprecipitation and then it was coated with silica following a sol-gel route. The material was characterized XRD analysis, SEM. The aqueous dispersion stability was investigated using dynamic light scattering.

Chapter-2

EXPERIMENTAL

2.1. Chemicals

The chemicals used for the synthesis of silica coated Fe_3O_4 magnetic nanoparticle were:

1. Anhydrous $FeCl_3$ and $FeSO_4$
2. Trisodium citrate and NH_4OH
3. tetra ethyl orthosilicate (TEOS)

2.2. Synthesis of Fe_3O_4 magnetic Nanoparticles:

0.648g of $FeCl_3$ and 0.548g of $FeSO_4.6H_2O$ were taken to which 40-45 ml of Millipore water was added under N_2 environment.5-10 ml of 25% NH_3 was added to the reaction mixture with continuous stirring and under nitrogen environment. And was kept for further stirring for1hr. 100 ml of 0.3 molar trisodium citrate was added to the reaction mixture and again was allowed for stirring for another 30 min at 90 ^{0}C. The synthesized particles were collected using magnetic separator and was washed with (3×20 ml) Millipore water. Fe_3O_4 were again dispersed in Millipore water [15].

2.3. Synthesis of silica coated Fe_3O_4 nanoparticles:

4g of the Fe_3O_4 despersed in Millipore water was taken in a solution of CH_3OH (160 ml) and 40 ml H_2O. To this reaction mixture 3ml of NH_3 solution and 2ml of tetraethyl orthosilicate(TEOS) were added one after another and was kept for stirring for further 24hr followed by washing with (2×30)ml Millipore water. Then dried at 80 ^{0}C and further heated at 400 ^{0}C [15].

2.4. Characterization

The identification of crystalline phase of the synthesized ferrite particles was performed by an Expert Pro Phillips X-ray diffractometer. The morphology and microstructure were analysed using scanning electron microscope (HITACHI COM-S-4200). The hydrodynamic size and dispersion stability of particle aggregates were investigated through dynamic light scattering using a Malvern ZS90 zetasizer. Hydrodynamic size was measured by dispersing 0.1 mg of sample in 1 ml phosphate buffered saline. The surface charge was determined through zeta

potential measurements. The surface chemistry of the nanoparticles was studied using FTIR spectroscopy (Perkin Elmer (BX 12).

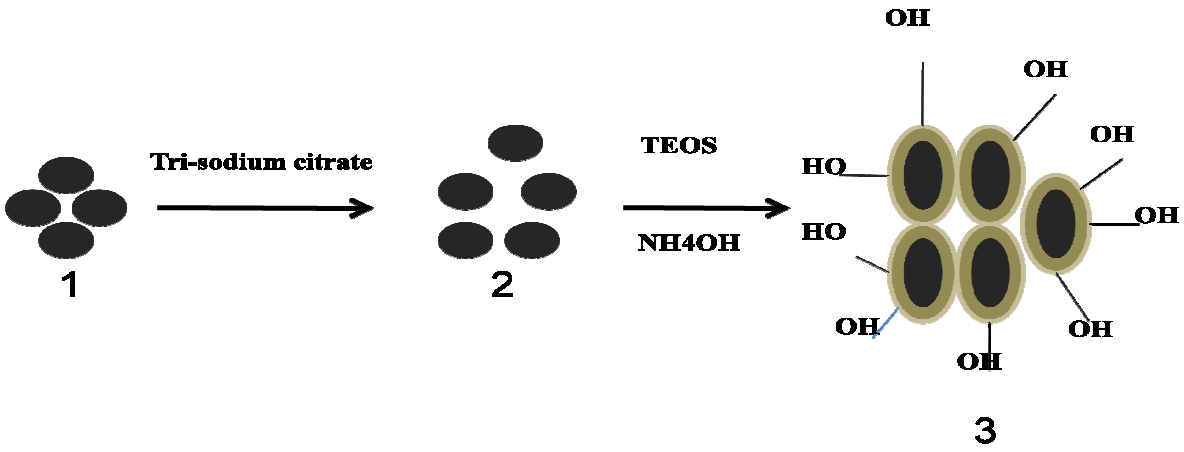

Figure1 Schematic presentation of the synthesis of silica coated magnetite nanoparticle

Chapter-3

RESULT AND DISCUSSION

3.1. Chemical reactions involved:

The chemical reaction for Fe3O4 precipitation is given by

$$2FeCl_3 + FeSO_4 + 8OH^- \xrightarrow{N_2\ gas} Fe_3O_4 \downarrow + 4H_2O$$

(black in color)

When Non-oxidising oxygen free environment is present

$$Fe_3O_4 + 0.25\,O_2 + 4.5\,H_2O \longrightarrow 3Fe(OH)_3 \downarrow$$

When inert condition is absent (red in colour)

The complete reaction is expected in between pH 9 to 14 while keeping the molar ratio of Fe^{3+} to Fe^{2+}= 2:1 under a non-oxidizing inert environment. If inert environment is not maintained properly then the Fe_3O_4 gets oxidized to red precipitate of $Fe(OH)_3$. As a result the physical and chemical properties of magnetic nanoparticles get affected. So to prevent its further oxidation to unexpected product and agglomeration the reaction is carried out under inert environment. The formation of silica coating occurs through condensation of $Si(OH)_4$ formed by base hydrolysis of tetraethylorthosilicate.

3.2. Characterizations:

3.2.1. XRD:

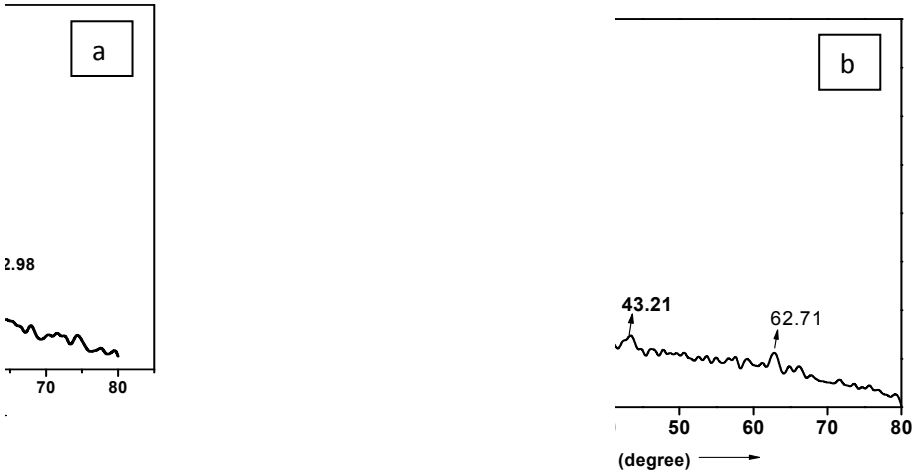

Figure 2 X-ray diffraction pattern of (a) as synthesized Fe_3O_4 (b) Silica coated Fe_3O_4

Table 1. 2Ɵ, d and corresponding [h k l] values of synthesized Fe_3O_4 nanoparticles

2Ɵ	30.3	35.7	43.5	53.7	57.5	62.9
D	2.96	2.53	2.09	1.71	1.61	1.48
[h k l]	[220]	[331]	[400]	[422]	[511]	[440]

Figure 1 illustrates the XRD patterns of black precipitations of Fe_3O_4 of magnetic particles. The position and relative intensity of all diffraction peaks match well with those of the magnetite (JCPDS 19-629) and broad peaks indicates nano-crystalline nature of the particles. Figure 2 shows XRD pattern of silica coated Fe_3O_4 magnetic nano-particle, the broad peak is due to amorphous silica. Thus XRD pattern indicates the presence of amorphous silica coating on magnetite nanoparticles surface. The broadened peak at 10-20 degree corresponds to SiO_2 and the rest of peaks are as those in XRD patterns of Fe_3O_4.

3.2.2. SEM: The spherical morphology of silica coated Fe_3O_4 magnetic nanoparticle was identified by scanning electron microscopy as shown figure2. From which the particle size was estimated to be approximately 200nm. From particle size determination the size of particle was found to be 232 nm from Figure 3.1 and that of magnetite core particle was found to be 148 nm from Figure 3.2.

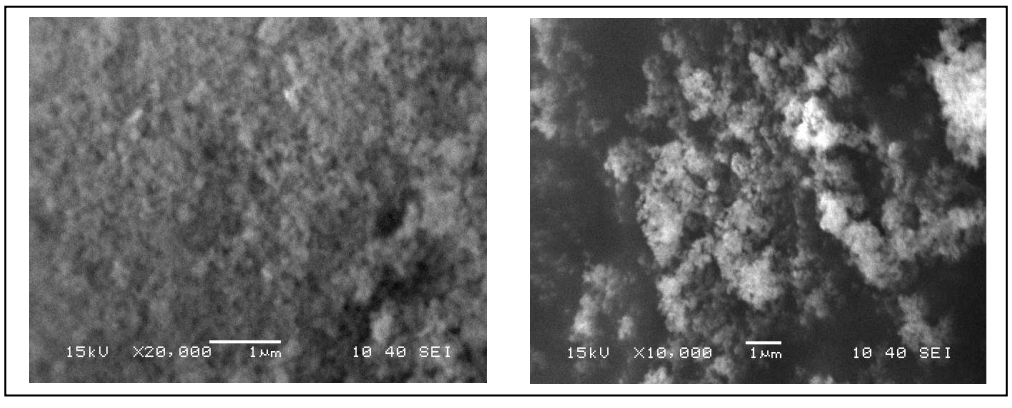

Figure 3: SEM images of silica coated Fe_3O_4 magnetic nanoparticle

3.2.3. Particle size by DLS:

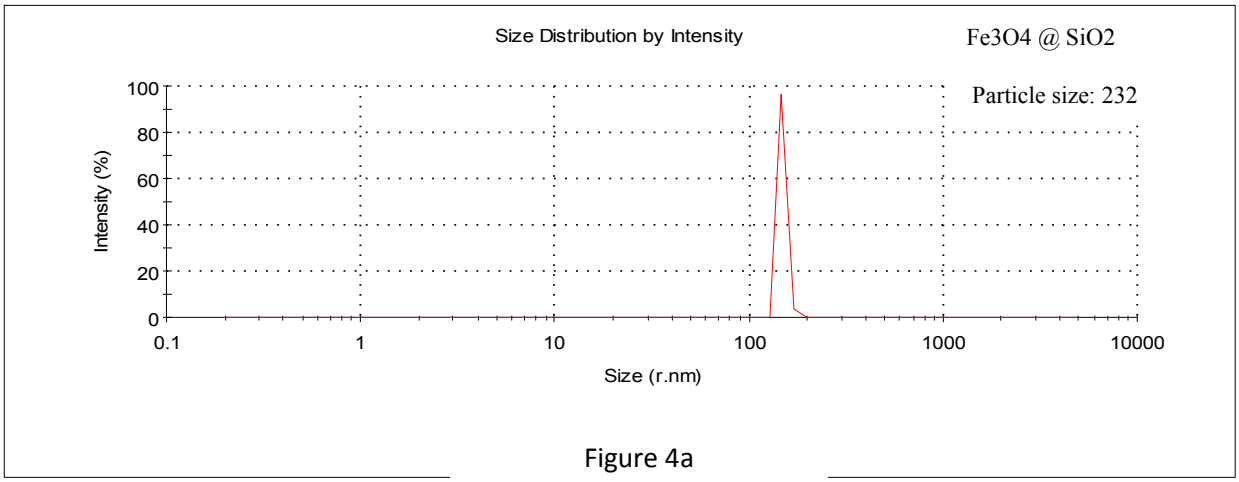

Figure 4a

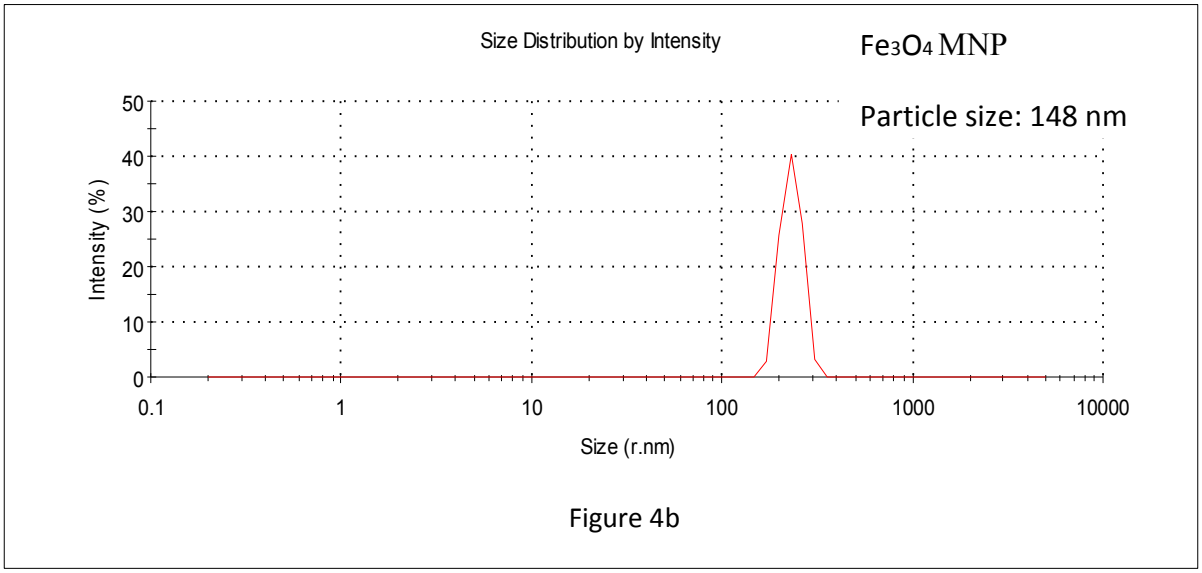

Figure 4b

3.4. FTIR:

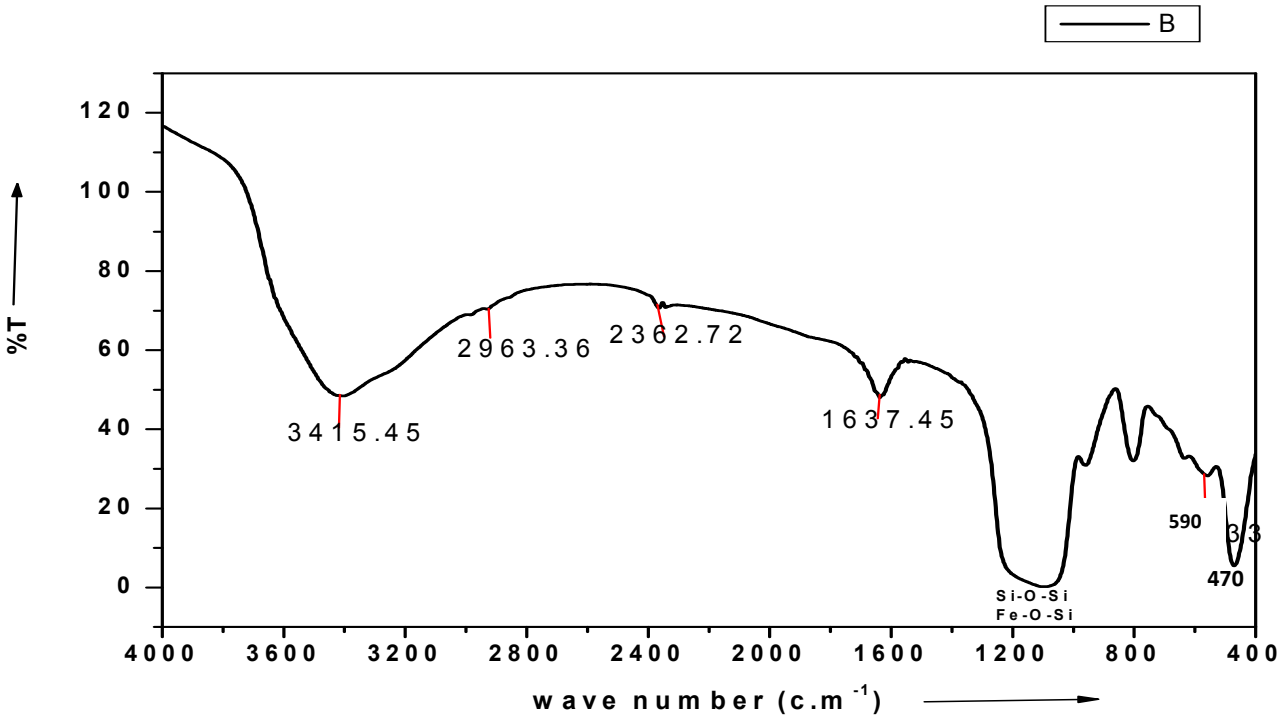

Figure 5

Figure 5 illustrates the FTIR spectrum of the silica coated magnetite nanoparticle. In case of bulk magnetite, the vibrational stretching band of Fe-O appears at 570 and 375 cm^{-1}, however in our case Fe-O vibration bands have shifted to 590 and 470 cm^{-1}. This blue shift in case of nanoparticles is a consequence of quantum confinement. The peaks at 3650cm^{-1}- 3200cm^{-1} shows the presence of O-H bond stretching, the broad peak in range 1050 cm^{-1}-1250 cm^{-1} might be due to overlapping of peaks corresponding to Si-O-Si and Fe-O-Si. The peak at 2362 is due to the presence of atmospheric CO_2.

Chapter-4

Conclusion

A systematic study of the formation of silica coated magnetite nanoparticle via co-precipitation method was successfully made. The result shows that the reaction parameters such as the volume ratio of alcohol/water, the amount of aqueous ammonia and TEOS influence the formation of silica coating on magnetic nanoparticles. Silica-coated magnetic nanoparticle of size 232 nm with spherical morphology could be conveniently prepared in large scale using the developed process. The amount of catalyst (ammonia aqueous) plays an important role on the formation of silica coated magnetic nanoparticles. By increase in amount of precursor (TEOS) larger silica-coated magnetic particles with more regular shape and monodispersed could be produced.

REFFERENCE:

[1] I. Prigogine, A. Stuart, in: J.L. Darmann, D. Fiorani, E. Ronc (Eds.), Advance in Chemical Physics, Wiley, New York, (**1977).**

[2] Y.H. Deng, C.C. Wang, J.H. Hu, Wu-Li Yang, S.K. Fu, Colloids and Surfaces A: Physicochemical. Eng. Aspects **262 (2005) 87–93**

[3] Aranzazu del Campo,Tapas sen,Jean-Paul lellouche,Ian J.Bruce,journal of magnetismand magneti materials 293 **(2005) 33-40**

[4] A.S. Lubbe, C.C. Alexiou, et al., J. Surg. Res. **95 (2001) 200.**

[5] A.L. Paul, G.R. Chandra, et al., J. Magn. Magn. Mater. **225 (2001) 301.**

[6] J. Halavaara, P. Tervahartiala, et al., Acad. Radiol**. 43 (2002) 180**.

[7] M. Mary, in: U. Hafeli, W. Schutt, M. Zborowski (Eds.), Scientific and Clinical Applications of Magnetic Carriers, Plenum Press, NewYork, **1997**

[8] A. Elaissari, M. Rodrigue, et al., J. Magn. Magn. Mater. **225 (2001)127.**

[9] A.n.d. Campoa,b,1,Tapas Sena,Jean-Paul Lellouchec,Ian J. Bruce Journal of Magnetism and Magnetic Materials **293 (2005) 33–40**

[10] X.G. Li, S. Takahashi, K. Watanabe, Y. Kikuchi, M. Koishi, Fabrication and characteristististics of Fe3O4-polymer composite particles by hybridization, Powder Technol. **133 (2003) 156–163.**

[11] H.X. Guo, X.P. Zhao, The synthesis of composite particles responsive to electric and magnetic fields, Opt. Mater. **22 (2003) 39**.

[12] G.L. Qiu, Y.L. Li, G.L. Siri, S.Y. Li, Sci. Technol. Chem. Ind. **9 (2001) 15**.

[13] E.M. Denkbas, E. Kilicay, C. Birlikseven, E. Ozturk, Magnetic chitosan microspheres: preparation and characterization, React. Funct. Polym**. 50 (2002) 225**

[14] Y. H. Deng, C.C. Wang, J.H. Hu, W.L. Yang, S.K. Fu .Colloids and Surfaces A: Physicochemical. Eng. Aspects 262 **(2005) 87–93**

[15] S.Mohapatra, D.Pal ,S.K. Ghosh [2],and P.Pramanik,design of superparamagnetic iron oxide nanoparticle for purification of recombinant proteins,journal of nanoscience and nanotechnology**,vol.7,(2007)1-7**